

Examining Co-Based Nanocrystals on Graphene Using Low-Voltage Aberration-Corrected Transmission Electron Microscopy

Jamie H. Warner,^{†,*} Mark H. Rummeli,[‡] Alicja Bachmatiuk,[‡] Mark Wilson,[§] and Bernd Büchner[‡]

[†]Department of Materials, University of Oxford, Parks Rd, Oxford, OX1 3PH, United Kingdom, [‡]IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany, and [§]Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

ABSTRACT We present a method to produce graphene and few layer graphene sheets using solution phase chemistry, which are used as ultrathin support membranes for enhanced imaging of nanomaterials using transmission electron microscopy. We demonstrate this by decorating the surface of the graphene sheets with Co-based nanocrystals (CoCl₂ and hcp Co). Low-voltage aberration-corrected high resolution transmission electron microscopy at 80 kV is used to image the nanocrystals on the thin graphene supports. We show that electron beam irradiation causes the CoCl₂ nanocrystals to become mobile on the graphene surface and exhibit both rotational and translational motion. We provide real-time *in situ* monitoring with atomic resolution of the coalescence of two CoCl₂ nanocrystals on the graphene surface, driven by electron beam irradiation. The CoCl₂ nanocrystals are then annealed in vacuum and transform into Co nanocrystals with hcp crystal structure. We show that these Co nanocrystals are catalytic and electron beam irradiation leads to the etching of the graphene surface, not observed for the CoCl₂ nanocrystals.

KEYWORDS: graphene · nanocrystals · aberration-corrected · HRTEM · cobalt

Graphene exhibits remarkable electronic transport and mechanical properties that make it attractive for a wide range of applications and have led to a recent dramatic surge in interest.¹ The properties of graphene can be extended by integrating it with other nanomaterials to form unique hybrid materials.^{2–4} One approach is to decorate the surface of graphene sheets with nanocrystals.^{5–8} This can lead to graphene–nanocrystal hybrids with enhanced properties such as electrocatalytic activity.⁵ Muszynski *et al.* recently decorated the surface of graphene sheets with gold nanoparticles.⁷ Graphene oxide sheets have also been coated with silver nanoparticles.⁹ Developing simple techniques to place a wide range of nanocrystal types on the surface of graphene is a key step toward the expansion of this area and further development of graphene-based novel nanocomposites.

Novel transmission electron microscopy support grids fabricated from carbon nanotube arrays have been recently produced by Zhang and co-workers and shown to give improved imaging performance of nanoparticles.¹⁰ Ultrathin graphene sheets also have the functionality of operating as a support for molecules and small nanomaterials in high resolution transmission electron microscopy (HRTEM) investigations.¹¹ The contrast from the graphene sheet is uniform because of the periodic lattice structure and also quite weak because of the limited number of atoms. Imaging small molecules or nanomaterials made from light elements is often inhibited by the random background signal of the amorphous carbon grids typically used in HRTEM. Meyer *et al.* recently showed that individual light atoms such as carbon and hydrogen could be imaged on the surface of graphene membranes, demonstrating the effectiveness of graphene as a support for TEM analysis.¹¹ However, the production of these types of graphene supports on TEM grids requires an elaborate procedure that involves mechanical exfoliation using scotch tape, transference to a silicon substrate with thin SiO₂ surface layer, characterization using optical spectroscopy or AFM, and then transference to specialized TEM grids. Lee and co-workers have shown the ability to image the soft–hard interface between gold nanoparticles and the citric acid stabilizers, using graphene as the support for HRTEM analysis.¹² In this case the graphene supports were synthesized using a substrate-free gas-phase procedure.¹³ Developing a simpler method for producing graphene supports for TEM is crucial for

*Address correspondence to
jamie.warner@materials.ox.ac.uk

Received for review October 6, 2009
and accepted December 10, 2009.

Published online December 18, 2009.
10.1021/nn901371k

© 2010 American Chemical Society

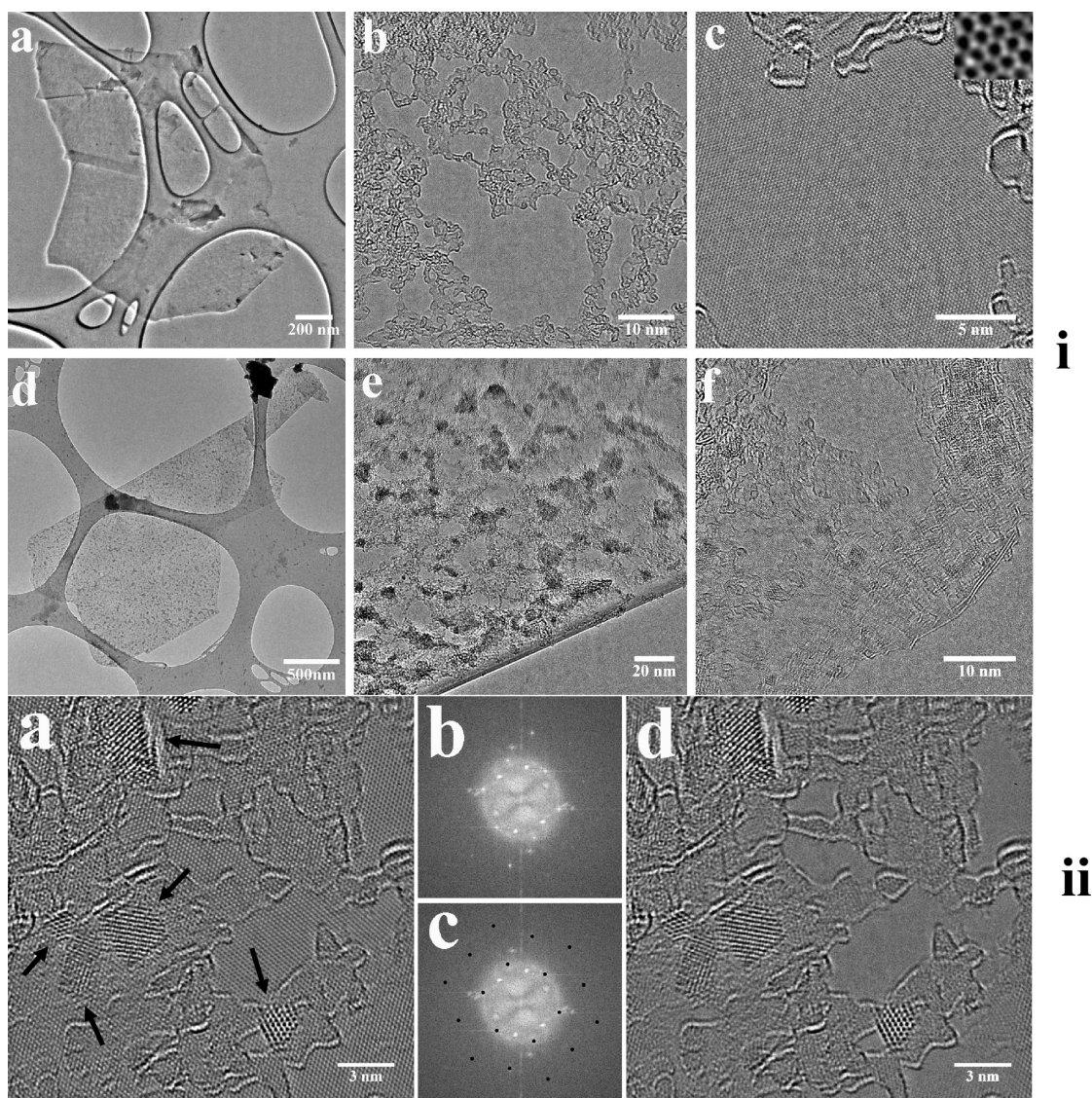


Figure 1. (i) (a) TEM image of a graphene sheet on a lacey carbon TEM grid; (b) higher magnification TEM image of the surface of a graphene sheet; (c) HRTEM image of the surface of a graphene sheet showing atomic lattice structure; (d) TEM image of a graphene sheet decorated with CoCl_2 ; (e) higher magnification TEM image of the surface of a graphene sheet decorated with CoCl_2 ; (f) HRTEM image of the surface of a graphene sheet decorated with CoCl_2 . (ii) (a) HRTEM of CoCl_2 nanocrystals on the surface of a graphene sheet, indicated with arrows; (b) 2D FFT of panel ii,a; (c) mask applied to 2D FFT to remove graphene lattice contributions, black spots indicate regions blocked out; (d) reconstructed HRTEM image generated from the 2D FFT mask in panel ii,c, with graphene atomic structure removed.

wider accessibility and expansion of the use of graphene as a support for TEM analysis of molecules and small nanomaterials.

Here, we show a simple method to prepare graphene sheets that are suitable as supports for growing nanocrystals on the surface and their examination using TEM. We decorate the surface of the graphene sheets with CoCl_2 to form a graphene–nanocrystal hybrid. CoCl_2 has been previously intercalated with graphite to form a novel quasi-two-dimensional magnetic system.¹⁴ The CoCl_2 nanocrystals are transformed into Co nanocrystals by annealing under dynamic vacuum. Low-voltage HRTEM equipped with spherical aberration correction at an accelerating voltage of 80 kV is used to image the atomic structure of the nanocrystals. We

examine the effect electron beam irradiation has on the interaction of CoCl_2 and Co nanocrystals with the graphene sheet and its surface.

RESULTS AND DISCUSSION

Figure 1i,a shows a typical few-layer graphene sheet consisting of 1–10 layers situated on the lacey carbon-coated TEM grid.^{15,16} Figure 1b shows a higher magnification TEM image of the surface of the graphene sheet. Small pieces of carbon partially cover the surface of the sheet. These small carbon pieces arise during the exfoliation process and are small fragments of graphene left on the surface. The atomic structure of these small fragments was imaged with HRTEM and showed graphitic sp^2 configuration and confirmed they

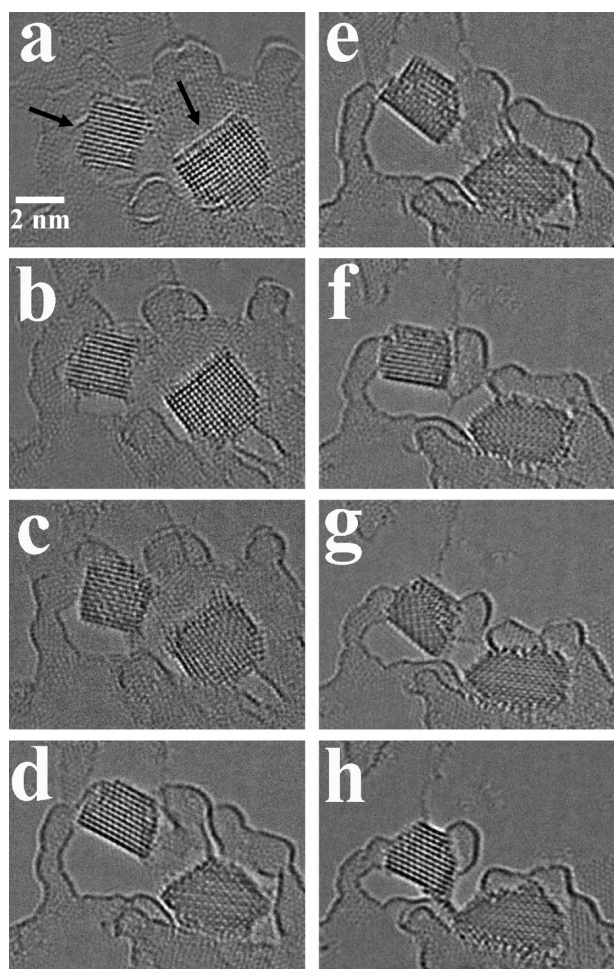


Figure 2. Time-series of HRTEM images showing motion of two CoCl_2 nanocrystals on the surface of graphene sheets, with graphene lattice structure removed by 2D FFT filtering. Time between frames is 10 s. CoCl_2 nanocrystals indicated with arrows.

were primarily graphene fragments, rather than large amounts of amorphous carbon. Figure 1i,c shows a HRTEM image of the graphene sheet with the sp^2 graphitic atomic structure resolved over a large region of $15 \text{ nm} \times 15 \text{ nm}$. The inset in the top right of Figure 1i,c shows atomic structure with individual carbon atoms resolved in the HRTEM image. The CoCl_2 nanocrystals were produced by depositing a solution of CoCl_2 in methanol onto the few layer graphene sheets. Figure 1i,d shows a graphene sheet after the deposition of CoCl_2 and the higher magnification TEM image in Figure 1i,e shows regions of dark contrast that were not previously present on the surface of the graphene sheet. Figure 1i,f presents a higher magnification TEM image of the surface of the graphene sheet decorated with CoCl_2 nanocrystals.

HRTEM analysis of the graphene sheets decorated with CoCl_2 showed small nanocrystals were formed with diameters ranging between 1 and 10 nm. Several of the nanocrystals were twinned and faceted. We found the CoCl_2 nanocrystals were generally surrounded by graphene fragments similar to those ob-

served in the original graphene sheet, Figure 1i,b. This suggests that the CoCl_2 nanocrystals often form in the voids between the graphene fragments on the surface as the methanol solvent dries. Figure 1ii,a shows a HRTEM image of CoCl_2 nanocrystals on the graphene surface with the nanocrystals indicated by arrows. The ultrathin nature of the few layer graphene sheets means that most of the contrast arises from phase contrast produced by interference effects from the periodic atomic structure. This well-defined structure can be easily removed from the HRTEM image by using 2D fast Fourier transforms (FFT) and appropriate filtering. The graphene lattice remaining after 2D FFT filtering is due to the small fragments that sit on top of the graphene support surface. These often do not stack AB, as expected for Bernal graphite stacking, and can have rotational twists with respect to the underlying layers. Thus the position of the lattice spots for these surface fragments does not coincide with the position of lattice spots for the underlying graphene support layer. We feel that it is not detrimental to leave the atomic structure of these surface graphene fragments since they do not overlap with the nanocrystal lattice fringes. It also enables us to see how the nanocrystals are attached to the graphene surface fragments.

Figure 1ii,b shows the 2D FFT from Figure 1ii,a with a large number of spots observed. The FFT from the graphene lattice has six spots in a hexagonal pattern with 0.21 nm distance. Other spots with smaller d -spacing are also observed.¹⁶ We removed all contributions of the graphene lattice by applying a mask to the 2D FFT, as shown in Figure 1ii,c. The black spots indicate areas that are removed. A reconstructed image is formed from the 2D FFT in Figure 1ii,c and is shown in Figure 1ii,d. The atomic structure of the supporting graphene sheet is now absent, with only the structure from the CoCl_2 nanocrystals and the surrounding graphene fragments remaining. This enables us to obtain a HRTEM image of the CoCl_2 nanocrystals as if they were suspended in vacuum with no background signal from the support. This demonstrates the capabilities of our graphene sheets as TEM support grids for imaging small nanocrystals with minimal background signal.

Electron beam irradiation of the CoCl_2 nanocrystals provided energy to drive both translational and rotational motion of the nanocrystals. Figure 2 presents an *in situ* time-series of HRTEM images showing the motion of two CoCl_2 nanocrystals. The time between frames is 10 s. The graphene lattice structure has been removed by applying a filter to the 2D FFT and reconstructing the image, as in Figure 1ii. Figure 2a shows two well-defined 2–3 nm faceted CoCl_2 nanocrystals, indicated with arrows, embedded among graphene fragments on the surface. As time progresses toward Figure 2d the nanocrystal on the left-hand side has moved upward and rotated. By Figure 2f the nanocrystal on the left-hand side has moved back down

and further rotated. Throughout the sequence in Figure 2 it can be seen that the nanocrystal on the left-hand side has a graphene fragment attached to its left-hand side that adjusts its shape as the nanocrystal moves around, acting like an anchor to prohibit extensive motion. The nanocrystal on the right-hand side stays surrounded by graphene fragments. These results demonstrate that CoCl_2 nanocrystals are mobile on the surface of the graphene sheets. The nanocrystals interact with the surrounding graphene fragments and this influences the dynamics of motion. The amount of graphene fragments surrounding the CoCl_2 nanocrystals decreases between Figure 2 panels a and h, and this is attributed to electron beam induced sputtering. The edges of the graphene fragments contain carbon atoms with dangling bonds and this lowers the threshold for electron beam induced sputtering.¹⁷

We also observed coalescence of CoCl_2 nanocrystals driven by electron beam irradiation. *In-situ* TEM has been previously used to examine the low-temperature unification of 10 nm PbSe nanocrystals through rotations and relaxations.¹⁸ Figure 3 shows an *in situ* time-series of HRTEM images of the two CoCl_2 nanocrystals originally presented in Figure 2 after further continuation of electron beam irradiation. The time between Figure 2h and Figure 3a is 10 s. The time between frames in Figure 3 is 10 s. The graphene atomic structure has been removed from Figure 3 by filtering the 2D FFT and forming a reconstructed image. The removal of a substantial amount of the surrounding graphene fragments provides sufficient room for the two nanocrystals to move toward each other and come in contact. As time progresses, Figure 3a–h, the two CoCl_2 nanocrystals coalesce and an overall structural re-configuration of the atomic structure occurs. By the end, Figure 3h, a single larger nanocrystal is formed from the two smaller nanocrystals. The coalescence of the nanocrystals indicates that the electron beam provides energy to heat this region and enable continual atomic rearrangement and the formation of a uniform crystal structure.

The graphene sheets decorated with CoCl_2 nanocrystals were annealed under dynamic vacuum at 320 °C for 2 h. This resulted in significant changes to the nanocrystals decorating the graphene surface. Figure 4 panels a and b show TEM images of the surface of the graphene sheets after the annealing. It is immediately apparent that well-defined spherical nanocrystals with strong contrast have been formed. Figure 4c shows a HRTEM image of the spherical nanocrystals on the graphene sheets. A HRTEM image of a single Co nanocrystal is shown in Figure 4d with resolved lattice structure. The crystal structure of the Co nanocrystal was examined using a 2D FFT, shown in Figure 4e. Six spots in hexagonal arrangement are observed with a *d*-spacing of 0.21 nm. This matches the [100] plane of

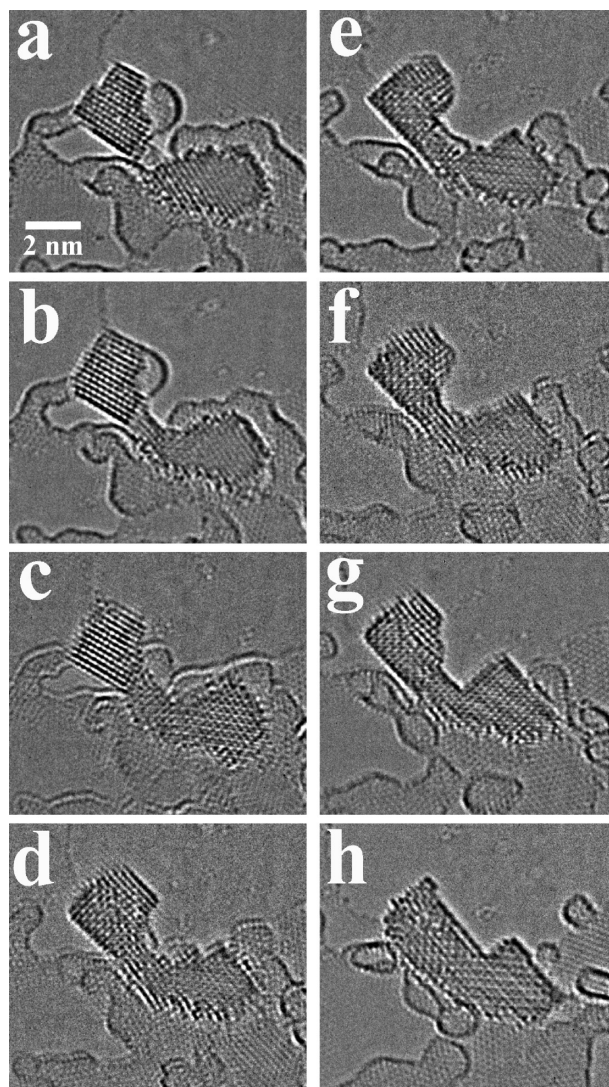


Figure 3. Time-series of HRTEM images showing the coalescence of two CoCl_2 nanocrystals on the surface of a graphene sheet. Graphene lattice is removed using 2D FFT filtering. Time between images is 10 s.

the hexagonal close-packed crystal structure of cobalt.¹⁹

When examining the Co nanocrystals using HRTEM there was a noticeable difference in the way they interacted with the graphene sheets compared to the CoCl_2 nanocrystals. We found that the Co nanocrystals etched away regions of the graphene surface, which the CoCl_2 nanocrystals did not. Co nanocrystals are known to be catalytic and recent reports have shown catalytic particles are capable of forming tracks in graphene sheets through an etching process.^{20–22} The etching process usually occurs by catalytic nanoparticles in contact with the edge one or more layers eating away the carbon and leaving a trail behind. Figure 5 shows an *in situ* time-series of HRTEM images of a Co nanocrystal on the surface of a few-layered graphene sheet. The time between frames is 15 s. Gold color is overlaid onto the HRTEM images in Figure 5 to indicate the regions that have been etched away. The edges of the region in the

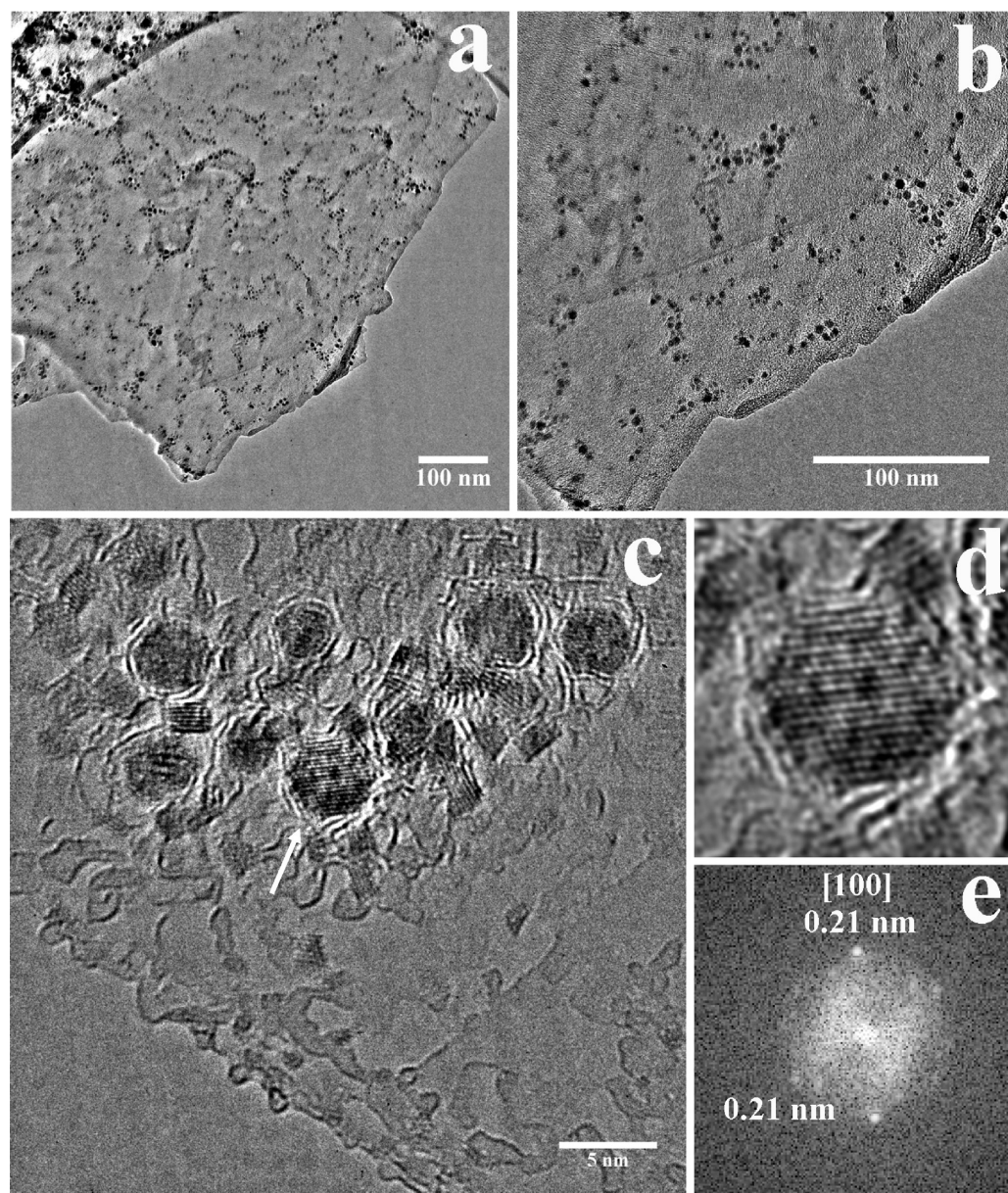


Figure 4. (a) TEM image showing Co nanocrystals on the surface of graphene sheets after high temperature annealing; (b) higher magnification of Co nanocrystals on surface of graphene sheets; (c) TEM image showing several Co nanocrystals with crystalline lattice structure near the edge of a graphene sheet; (d) HRTEM image of a Co nanocrystal, indicated with an arrow in panel c; (e) FFT of panel d showing lattice spots associated with [100] hcp Co structure.

graphene layer that has been removed by the nanoparticle produces strong contrast and enables the etching process to be tracked. Figure 5a shows a spherical 2 nm Co nanocrystal at the beginning of electron beam irradiation. By Figure 5d the Co nanocrystal has moved upward and has reorganized its shape into a crescent moon in order to maximize its contact area with the edge of the sheet it is etching. At this stage the Co nanocrystal must be embedded within the few-layer graphene sheet and as it moves sideways it etches away the carbon. During the etching process the Co nanocrystal does not appear to be highly crystalline, and this may reflect the nature of the etching process and the way carbon is incorporated.

We found that the smaller Co nanocrystals were more reactive with the graphene surface than larger ones. Furthermore, the etching produced by the Co nanocrystals was often short-lived and the Co nanocrystals seemed to lose their ability to etch away the graphene surface. It is possible that the removal of graphitic carbon by the Co nanocrystals occurs through the conversion into gases such as methane or carbon dioxide.²² Thus it is the presence of trace amounts of hydrogen and oxygen on the surface of the graphene sheets or on the Co nanocrystals that assists the etching process. We attribute the loss of catalytic behavior of the Co nanocrystals to the depletion of hydrogen or oxygen in the local environment of the Co nanocrystals

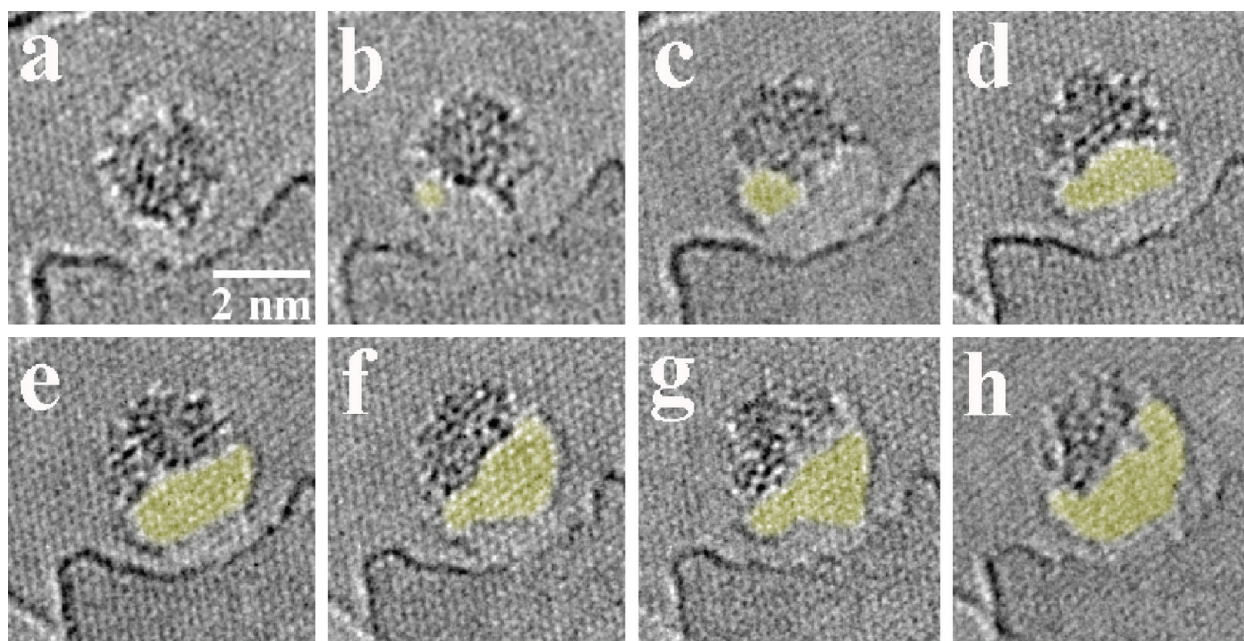


Figure 5. Time-series of HRTEM images showing the catalytic etching behavior of Co nanocrystals on the surface of a few layer graphene sheet. Time between frames is 15 s. Region colored in yellow indicates area of surface that has been etched away.

during the etching process. This could be further explored using environmental HRTEM experiments. However, we believe that we have conclusively demonstrated the proof-of-principle result that the Co nanocrystals presented in Figures 4 and 5 exhibit catalytic etching of graphene sheets. This behavior is not present in the case of the original CoCl_2 nanocrystals and confirms that our observations are linked directly to the composition of the nanocrystals and required the combination of Co nanocrystals and electron beam irradiation. It may also be possible that a cobalt carbide phase is formed during the etching process that leads to loss of catalytic activity.

CONCLUSION

We have shown a very simple method for decorating graphene sheets with CoCl_2 nanocrystals. We

showed that the thin nature of the graphene sheets enabled their use as nearly transparent grids for HRTEM analysis. *In-situ* real-time HRTEM examination of the CoCl_2 nanocrystals revealed they exhibit translational and rotational movement across the surface of graphene and eventually coalescence together to form a single crystalline species. These CoCl_2 were transformed into Co nanocrystals by a straightforward annealing under dynamic vacuum. The Co nanocrystals displayed unique interactions with the surface of the graphene sheets that lead to etching. The technique presented here where graphene sheets are decorated with nanocrystals or other molecular compounds can be easily extended to other materials such as ferrocene or fullerenes. This approach holds great promise for utilizing graphene sheets as support membranes for HRTEM analysis of weak contrast molecules.

EXPERIMENTAL METHODS

Graphene sheets were prepared using a previously reported method of ultrasonically exfoliating highly ordered pyrolytic graphite (HOPG) in a solution of 1,2-dichloroethane for 1 h.¹⁵ This resulted in the chemical exfoliation of sheets of graphene consisting of 1–10 layers. The solution is left to rest for 1 h after which the large graphite pieces have settled to the bottom. The top 10% of the supernatant is removed with a pipet and placed in a clean separate vial. A drop of the solution containing the graphene sheets in 1,2-dichloroethane is deposited onto lacey carbon-coated TEM grids and allowed to dry. In a separate vial, 1 mg of CoCl_2 was added to 5 mL of methanol and sonicated for 30 min to form a clear solution. A drop of this CoCl_2 solution was deposited onto a TEM grid that already contained the predeposited graphene sheets and allowed to dry. This resulted in CoCl_2 nanocrystals decorated across the surface of the graphene sheets. After examination with HRTEM the TEM grid contain-

ing the graphene sheets decorated with CoCl_2 was annealed at 320 °C for 2 h under a vacuum of 1×10^{-6} mbar. This resulted in the transformation of the CoCl_2 nanocrystals into Co nanocrystals with hcp crystal structure. HRTEM was performed using an aberration corrected FEI Titan³ operating at 80 kV.

Acknowledgment. J.H.W. thanks the Glasstone Fund and Brasenose College, Oxford, for support.

REFERENCES AND NOTES

- Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.
- Zhang, X.; Huang, Y.; Wang, Y.; Ma, Y.; Liu, Z.; Chen, Y. Synthesis and Characterization of a Graphene- C_{60} Hybrid Material. *Carbon* **2009**, *47*, 334–337.
- Tung, V. C.; Chen, L.-M.; Allen, M. J.; Wassei, J. K.; Nelson, K.; Kaner, R. B.; Yang, Y. Graphene-Carbon Nanotube Hybrid Materials for High-Performance Transparent Conductors. *Nano Lett* **2009**, *9*, 1949–1955.

- Su, Q.; Pang, S.; Alijani, V.; Li, C.; Feng, X.; Mullen, K. Composites of Graphene with Large Aromatic Molecules. *Adv. Mater.* **2009**, *21*, 3191–3195.
- Yoo, E.; Okata, T.; Akita, T.; Kohyama, M.; Nakamura, J.; Honma, I. Enhanced Electrocatalytic Activity of Pt Subnanoclusters on Graphene Nanosheet Surface. *Nano Lett.* **2009**, *9*, 2255–2259.
- Wang, D.; Choi, D.; Li, J.; Yang, Z.; Nie, Z.; Kou, R.; Hu, D.; Wang, C.; Saraf, L. V.; Zhang, J.; *et al.* Self-Assembled TiO₂-Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion. *ACS Nano* **2009**, *3*, 907–914.
- Muszynski, R.; Seger, B.; Kamat, P. V. Decorating Graphene Sheets with Gold Nanoparticles. *J. Phys. Chem. C* **2008**, *112*, 5263–5266.
- Williams, G.; Seger, B.; Kamat, P. V. TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* **2008**, *2*, 1487–1491.
- Lu, G.; Mao, S.; Park, S.; Ruoff, R. S.; Chen, J. Facile, Noncovalent Decoration of Graphene Oxide Sheets with Nanocrystals. *Nano Res.* **2009**, *2*, 192–200.
- Zhang, L.; Feng, C.; Chen, Z.; Liu, L.; Jiang, K.; Li, Q.; Fan, S. Superaligned Carbon Nanotube Grid for High Resolution Transmission Electron Microscopy of Nanomaterials. *Nano Lett.* **2008**, *8*, 2564–2469.
- Meyer, J. C.; Girit, C. O.; Crommie, M. F.; Zettl, A. Imaging and Dynamics of Light Atoms and Molecules on Graphene. *Nature* **2008**, *454*, 319–322.
- Lee, Z.; Jeon, K.-J.; Dato, A.; Erni, R.; Richardson, T. J.; Frenklach, M.; Radmilovic, V. Direct Imaging of Soft-Hard Interfaces Enabled by Graphene. *Nano Lett.* **2009**, *9*, 3365–3369.
- Dato, A.; Radmilovic, V.; Lee, Z.; Phillips, J.; Frenklach, M. Substrate-Free Gas-Phase Synthesis of Graphene Sheets. *Nano Lett.* **2008**, *8*, 2012–2016.
- Elahy, M.; Dresselhaus, G. CoCl₂-Intercalated Graphite: A Quasi-Two-Dimensional Magnetic System. *Phys. Rev. B* **1984**, *30*, 7225–7235.
- Warner, J. H.; Rummeli, M. H.; Gemming, T.; Büchner, B.; Briggs, G. A. D. Direct Imaging of Rotational Stacking Faults in Few Layer Graphene. *Nano Lett.* **2009**, *9*, 102–106.
- Warner, J. H.; Schaffel, F.; Rummeli, M. H.; Büchner, B. Examining the Edges of Multi-Layer Graphene Sheets. *Chem. Mater.* **2009**, *21*, 2418–2421.
- Girit, Ç. ö.; Meyer, J. C.; Erni, R.; Rossell, M. D.; Kisielowski, C.; Yang, L.; Park, C.-H.; Crommie, M. F.; Cohen, M. L.; Louie, S. G.; Zettl, A. Graphene at the Edge: Stability and Dynamics. *Science* **2009**, *323*, 1705–1708.
- van Huis, M. A.; Kunneman, L. T.; Overgaag, K.; Xu, Q.; Pandraud, G.; Zandbergen, H. W.; Vanmaekelbergh, D. Low-Temperature Nanoscale Unification Through Rotations and Relaxations Probed by *in Situ* Transmission Electron Microscopy. *Nano Lett.* **2008**, *8*, 3959–3963.
- Petit, C.; Wang, Z. L.; Pileni, M. P. Seven-Nanometer Hexagonal Close Packed Cobalt Nanocrystals for High-Temperature Magnetic Applications through a Novel Annealing Process. *J. Phys. Chem. B* **2005**, *109*, 15309–15316.
- Datta, S. S.; Strachan, D. R.; Khamis, S. M.; Johnson, A. T. C. Crystallographic Etching of Few-Layer Graphene. *Nano Lett.* **2008**, *8*, 1912–1915.
- Ci, L.; Xu, Z.; Wang, L.; Gao, W.; Ding, F.; Kelly, K. F.; Yakobson, B. I.; Ajayan, P. M. Controlled Nanocutting of Graphene. *Nano Res.* **2008**, *1*, 116–122.
- Konishi, S.; Sugimoto, W.; Murakami, Y.; Takasu, Y. Catalytic Creation of Channels in the Surface Layers of Highly Ordered Pyrolytic Graphite by Cobalt Nanoparticles. *Carbon* **2006**, *44*, 2338–2340.
- Schaffel, F.; Warner, J. H.; Bachmatiuk, A.; Rellinghaus, B.; Büchner, B.; Schultz, L.; Rummeli, M. H. Shedding Light on the Crystallographic Etching of Multilayer Graphene at the Atomic Scale. *Nano Res.* **2009**, *2*, 695–705.